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THE QUANTITATIVE SEPARATION AND DETERMINATION OF SUBSIDIARY DYES IN THE PERMITTED FOOD COLORS.

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Most simple commercial dyestuffs contain large amounts of subsidiary coloring matters. The percentage of such substances in the purer dyes intended for use in food products is a matter of some importance, as they may constitute the most objectionable of the impurities. Reasonably pure coloring matters are necessary in examining methods for the estimation of the subsidiary coloring matters. A brief description is here given of the pure colors employed in this work. All were made in the laboratory from "chemically pure" grade chemicals of high quality, unless otherwise stated. The dyes were given a second crystallization, or salting out, and seemed to be practically free from organic impurities.

Orange I.—From diazotized sulphanilic acid and α-naphthol.

Orange II.—From diazotized sulphanilic acid and β-naphthol.

Ponceau 3 R.—From diazotized 1-2-4-5-pseudo-cumidin (melting point, 63° C.) and commercial R-salt (sodium salt of 2-naphthol-3-6-disulphonic acid), the latter purified by boiling out with 80 per cent alcohol, and crystallizing from salt solution and from water.

Crocein Orange.—From diazotized anilin and commercial S-salt (sodium 2-naphthol-6-sulphonate), the S-salt purified by crystallizing from salt solution and from water.

Amaranth.—From diazotized naphthionic acid and R-salt prepared as stated for Ponceau 3 R.

Fast Red E.—From diazotized naphthionic acid, and S-salt, the latter similar to that used for Crocein Orange.

New Coccin.—From diazotized naphthionic acid and commercial G-salt (sodium salt of 2-naphthol-6-8-sulphonic acid) purified by crystallization from water.

DETERMINATION OF FAST RED E AND SIMILAR COLORS IN AMARANTH.

This separation is readily made by the procedure indicated in Bureau of Chemistry Circular 89. Treat the solution containing about 0.2 gram dye with 5 cc five-normal hydrochloric acid and

dilute to 50 cc. Then shake out with amyl alcohol, extracting in succession in three separatory funnels each containing 50 cc of the solvent. Wash the amyl alcohol portions in the funnels with 3 50 cc amounts of fourth-normal hydrochloric acid, these being passed through the series in the same order as was the original solution. Give the last two separators a fourth washing, the last one a fifth. Then dilute the amyl alcohol with gasoline, removing the Fast Red with very dilute caustic soda solution, and determining by the method of Knecht and Hibbert, using titanium trichlorid. With large amounts of Fast Red a series of four funnels must be used. In all cases it is essential that the liquids be thoroughly shaken together.

The results obtained by this method follow:

Determination of Fast Red in Amaranth.

Number of funnels.	Total dye taken.	Fast Red taken.	Fast Red recovered.
	Gram.	*Per cent.*	*Per cent.*
3	0.1644	0.0	0.15
3	.1737	5.3	5.2
3	.2107	22.0	21.3
4	.2107	22.0	22.0

Approximate figures may be obtained by diluting 2.5 cc of the 1 per cent solution of the dye with 30 cc of fiftieth-normal hydrochloric acid and shaking with 15 cc of amyl alcohol. The amyl alcohol is then compared colorimetrically with standards prepared in the same way, using pure dyes or those of known composition.

APPROXIMATE DETERMINATION OF NEW COCCIN AND SIMILAR DYES IN AMARANTH.

The following empirical method gives a measure of the amount of such colors present: Treat 50 cc of the 0.02 per cent solution of the color with 10 cc of tenth-normal benzidine solution (9.2 grams base per liter, in half-normal hydrochloric acid), mix the solution well and allow to stand exactly two minutes. Then filter through a folded filter and titrate 50 cc of the filtrate against titanium trichlorid. Blanks made up with known amounts of pure Amaranth and New Coccin are carried through at the same time. As Fast Red E and similar colors interfere, if this method has been used for their separation, the extracted solution and washings containing the Amaranth are combined and taken to dryness on the water bath to remove the acid and dissolved amyl alcohol. This evaporation does not affect the Amaranth.

Advantage may also be taken of the lability of the 6 sulpho-group in Amaranth, when warmed with potassium cyanid solution (see Lange, D. R. P. 189935 and 191838): Treat 20 cc of the 1 per cent

solution of the dye with solutions containing 1 gram each of potassium cyanid and ammonium chlorid, and make the volume to 45 cc. Heat the mixture for six minutes in a large test tube immersed in a boiling water bath. Then quickly cool and acidify by addition of 10 cc of concentrated hydrochloric acid. The Amaranth (color acid) is converted into sulpho-naphthalene-azo-2-naphthol-3-cyan-6-sulphonic acid, a maroon dye that may be separated from the unchanged new Coccin by a procedure similar to that described for Fast Red E. Some coloring matter is destroyed, and it is necessary to carry through blanks containing known amounts of the dyes.

DETERMINATION OF MONOSULPHONATED DYES IN PONCEAU 3 R.

The separation of the monosulphonated Orange dyes from Ponceau 3 R by means of amyl alcohol and dilute hydrochloric acid gives high results for the Orange, which becomes especially apparent when one of the colors is present in relatively small amount. This is due to the fact that the distribution ratio of Ponceau 3 R changes rather markedly with varying dye concentration, in dilute mixtures the color becoming relatively more soluble in the alcohol layer. Consequently it is practically impossible to wash out the last traces of Ponceau from the solvent containing the Orange. An accurate separation may be made, however, by using first dilute acid to remove the bulk of the Ponceau, completing the washing with 5 per cent sodium chlorid solution. The first washings with the salt water may contain some Ponceau in suspension, but the amount is so small that it does not interfere. It is hardly advisable to use hydrochloric acid of lower concentration than sixteenth-normal, as even at this strength the liquids separate rather slowly.

The monosulphonated dye present in commercial Ponceau 3 R is perhaps mainly sodium trimethylbenzene-azo-naphthol-sulphonate, derived from diazotized pseudo-cumidin and S-salt. Instead of this color, Crocein Orange was used in the work described below, a pure lot having been prepared some time previously for another purpose. Since with homologous dyes the relative solubility in amyl alcohol seems to increase with the molecular weight, a separation effective for Crocein Orange should be still more so for its homologues, although the differences here are insignificant.

A procedure similar to that described for Fast Red E was followed. The dye solution was treated with 2.5 cc five-normal hydrochloric acid diluted to 50 cc and then passed through three funnels each containing 50 cc amyl alcohol. Four 50 cc portions of sixteenth-normal acid were then passed in order through the separators, followed by three 50 cc portions of 5 per cent salt solution. The last two separators were washed with a fourth 50 cc portion of the

salt solution, the last one with a fifth. The dye was then removed as stated below.

Determination of Orange in Ponceau 3 R.

Total dye taken.	Orange taken.	Orange recovered.
Gram.	*Per cent.*	*Per cent.*
0.1867	0.0	0.2
.1961	4.8	5.0
.2339	20.5	20.2

DETERMINATION OF ORANGE II IN ORANGE I.

In the preparation of these dyes it is known that Orange I is much more soluble than Orange II in dilute sodium carbonate solution. They may be separated by a method similar to that described for Fast Red E, using amyl alcohol and 5 per cent sodium carbonate solution. The equilibrium between the concentrations of the Orange I in the two layers is not very quickly established, and the mixtures must be well shaken, then given some time to separate. The liquids can be very quickly separated with a centrifuge.

The following procedure furnished the data given. The dye solution (about 50 cc) was treated with 10 cc concentrated hydrochloric acid and shaken with 50 cc amyl alcohol. Practically all the dye went into the alcohol, and the lower layer was drawn off and discarded. The amyl alcohol was then washed with six 50 cc portions of normal or 5 per cent sodium carbonate, these being passed successively through a second and third funnel each containing 50 cc of amyl alcohol. The last two funnels were given two additional washings. Gasoline was then added, and the color removed and determined in the usual way.

The result given in the fourth line was obtained by the same procedure, except that a third funnel was not used.

Determination of Orange II in Orange I.

Total dye taken.	Orange II taken.	Orange II recovered.
Gram.	*Per cent.*	*Per cent.*
0.1605	0.0	0.3
.1708	5.7	6.0
.2095	23.4	22.6
.1708	5.7	5.5

Determined by these methods in the dyes intended for sale as food colors, Amaranth contains from 1 to 5 per cent lower sulphonated colors, and somewhat more New Coccin and similar dyes. Ponceau 3 R contains from 1 to 5 per cent lower sulphonated dyes, and Orange I, the same amount of Orange II.

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